

PREPARATION OF BLOCK POLYURETHANE-AMIDES

This Application claims the priority of Swiss No. 11,122/86, filed Mar. 20, 1986.

The present invention is directed to a process for the preparation of thermoplastic block polyurethane amides having polyurethane and polyamide portions which are connected by ester linkages. The invention also encompasses the use of such compounds in the formation of injection-molded and extruded bodies, as well as for hot melt adhesives.

BACKGROUND OF THE INVENTION

Since their discovery, polyamides have become a class of materials of increasing importance. They are now available in a multitude of modified forms and, in particular, as mixtures with various other polymers for a variety of uses. In order to enhance their usefulness, attempts have been made to integrate the advantageous properties of polyamides with those of polyurethanes by simple physical mixture of the respective polymers in the molten state. However, mixtures of this type generally exhibit poorer properties than the individual components because of the limited compatibility of the polyamides with polyurethanes.

In theory, another way in which to combine the properties of polyamides and polyurethanes in one product is by the construction of suitable block polymers in which alternating polyurethane and polyamide segments are connected with each other by chemical bonds. DE-AS-1,224,031 (BASF) gives examples in which polyether-polyol groups can be linked with low molecular polyamides carrying carboxyl or amino end groups via urethane and amide or urea groups. To this end, the polyether-polyol is first reacted with a molar excess (up to 2 mol) of diisocyanates and the isocyanate-modified polyether-polyol is reacted with the carboxyl-amino groups of the polyamides.

These products can be used, in small amounts, as anti-static additives for thermoplasts, especially polyamides. They are not suitable for thermoplastic processing; e.g. for injection-molded and extruded bodies. In the reaction of diisocyanates with polyamides which carry amino, hydroxyl or carboxyl terminal groups, there are usually side-reactions which very quickly lead to partial cross-linking of the resultant polymers of the type described in DE-AS-1,224,031, especially if these polymers are prepared at high temperatures in the melt. The cross-linking reactions which take place, e.g. as a result of the reaction of isocyanate with amide groups (which is difficult to control), can proceed so far that the polymers which are obtained block conventional injection molding machines, extruders, blowing and foil apparatus, because they can no longer be melted and worked. Therefore, they are wholly unsuitable for present-day thermoplast processing. Owing to their poor meltability and resultant poor flowability, polyamides modified with diisocyanates in accordance with DE-AS-1,224,031 also cannot be used as hot melt adhesives.

Also, in other linking reactions of polyamides with isocyanate-terminated polyurethanes, it is impossible to avoid the cross-linking which immediately ensues, and which leads to similarly unusable products. Thus, the object of the present invention is a process for the preparation of such thermoplastic processable block polymers with amide and urethane segments, which no

longer exhibit the disadvantage of comparable products previously known.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises a method for the preparation of block polyurethane amides in a melt by the reaction of

(a) a linear polyamide having terminal carboxylic acid ester groups and which melts at not more than 210° C.; and

(b) a polyurethane having terminal hydroxyl groups; at a temperature of 160° to 240° C., and in the presence of a transesterification accelerator. In preferred forms of the invention, the polyamide and polyurethane are present in substantially equimolar amounts and the reaction is carried out under reduced pressure. Prior to the condensation, it has been found advantageous to first blend the polyamide and polyurethane to form a homogeneous mixture above their respective melt temperatures. The reaction can be carried out as a batch process, e.g. in an autoclave, or as a continuous process, especially using thin-layer condensation. The number average molecular weight range of the polyamide is from 500 to 12000 g/mol; preferably, 900 to 5,000 g/mol.

The polyamide reactant is prepared from polyamide-forming components and a dicarboxylic acid, together with a mono-functional, primary aliphatic alcohol. Broadly, the components and the dicarboxylic acid are used in an amount sufficient to provide the second terminal carboxylic acid ester group in the polyamide and the alcohol is used in an amount sufficient to esterify the intermediate carboxyl groups. This reaction takes place in the presence of an esterification catalyst.

Appropriate polyamide-forming components are lactams and ω -amino carboxylic acids having 6 to 12 carbon atoms. In particular, caprolactam, laurilactam, dodecanolactam, aminocaproic acid, 11-aminoundecanoic acid, or 12-aminododecanoic acid (12-aminolauric acid), have been found advantageous. These polyamide-forming components may be substituted by equimolar amounts of a dicarboxylic acid having 6 to 13 carbon atoms and a diamine having 6 to 18 carbon atoms. Of course, such components can be used alone or with others.

To introduce the second terminal carboxylic acid ester group into the molecule of the polyamide reactant, dicarboxylic acids having 6 to 36 carbon atoms are used. In particular, adipic acid, terephthalic acid, isophthalic acid, azelaic acid, sebacic acid, dodecanedioic acid, brassidic acid, or dimerised fatty acids have been found particularly desirable.

The preferred aliphatic primary alcohols have 4 to 8 carbon atoms and include n-butanol, n-hexanol, n-octanol, and 2-ethyl-1-hexanol. The esterification catalysts are preferably Sn(II), Sn(IV), and Zr compounds. In particular, Sn(II) oxide, Sn(II) salts of monocarboxylic acids, dibutyltin oxide, n-butyltin acid, and Zr(OR)₄, wherein R is alkyl having 1 to 4 carbon atoms, have been found quite suitable. The esterification is preferably conducted under reduced pressure and at temperatures between 160° and 240° C.

The polyamides are prepared by a two-step reaction. First, the polyamide-forming components are reacted with the dicarboxylic acid to introduce the terminal carboxyl groups onto the polyamide base molecule. Thereafter, these groups are esterified by the primary